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Plastics Additives Handbook

5th Edition

Edited by Dr. Hans Zweifel

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Foreword

Adding Value to Polymers

Plastics without additives are not viable. Additives are essential to make thermoplastics processable and to improve end-use properties. Our lives would be very different today if plastics had not become the material of choice for many applications. With additives, we can shape the use of plastics, allowing exciting new products that have an impact on everyday life.

More than ten years have passed since the last major revision of the "Plastics Additives Handbook". During this decade the demands on additives have continued to evolve, not only because of more demanding processing conditions but also because plastics are being used in more sophisticated applications. Meeting these challenges has only been possible with a close cooperation between the polymer and additives industries.

This new, fully revised edition of the traditional Plastics Additives Handbook provides an excellent overview of the polymer additives industry. It offers guidance for all professionals involved in the development of new resin grades and novel end-use applications and will be an essential reference well into the new millennium.

On behalf of Ciba Specialty Chemicals, I would like to thank not only Dr. Hans Zweifel for composing this 5th edition but also all the specialists who have contributed in their field of expertise to make this Handbook a most valuable instrument for the plastics industry – not only today, but also tomorrow.

Discover with them the exciting world of polymer additives. Enjoy reading!

Felix K. Meyer

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12 Flame Retardants

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12.1 Introduction

The inherent flammability of many plastics, especially those with a high carbon content, requires that measures be taken to allow their safe use where the potential for fire exists. For many resins, the most cost effective method of increasing fire safety is to add a flame retardant additive [1] during processing.

The use of flame retarded, or ignition resistant, plastics may be required by regulation or can be specified by the user. The fact that flame retarded plastics diminish damage and decrease fatalities resulting from fires is readily established by looking at statistics related to television fires. It has been estimated [2] that in 1976, there were about 11,000 reported fires in the USA involving television sets. In 1992, this number had decreased to about 200, despite the far greater number of television sets in operation. A direct cause of this improvement in fire safety was the adoption of a voluntary standard to strengthen the ignition resistance of the television set. Flame retardant additives in the plastic television case and the interior circuit boards enabled manufacturers to meet the requirements of the voluntary standard.

The choice of flame retardant to use in a particular plastic is not arbitrary. Some flame retardants are too volatile and some are not volatile enough to function properly with a selected resin. One flame retardant may adversely affect the physical properties of a resin while another may not. Matching a flame retardant to a resin requires a knowledge of combustion chemistry as well as physical chemistry.

Unfortunately, the choice of flame retardant is also dependent upon which test a manufacturer is attempting to satisfy. Different countries have different tests and different flammability requirements. A flame-retarded product may be certified to be marketed in one country, but the same product may not meet the standards of another country. Harmonization of fire safety standards is truly an international problem.

Besides imparting ignition resistance, the ideal flame retardant should have a number of other attributes. It should be easy to incorporate and, by necessity, be compatible with the plastic. It should not severely alter the physical properties of the resin. It is preferably colorless, with good UV stability when needed, effective in small amounts, and inexpensive. Of particular importance is that the use of the additive should not result in the corrosion of processing equipment or expose workers or consumers to harmful dust, fumes, or odors.

Published information indicates that the sales of US flame retardants in 1995 were on the order of \$700 million (USD) [3]. A comprehensive study of the flame retardant industry is available from SRI Consulting [4].

12.2 Flame Retardant Mechanisms

Flame retardants generally impart their properties to plastics in the condensed or the gas phase. In the condensed phase, the additive can remove thermal energy from the substrate by functioning as a heat sink or by participating in char formation to form a barrier against heat and mass transfer. The additive can also provide flame retardancy by condensation, evaporation, or mass dilution or by participating in endothermic chemical reactions. Char-forming systems, also called intumescent systems, form a foamy, porous protective barrier on the plastic to shield it from further pyrolysis and combustion. Most intumescent systems require an acid source (catalyst), a char-forming compound (carbonific), and a gas-evolving compound (spumific). In a typical system, a phosphorus compound promotes the charring of a substrate (typically a carbon-oxygen compound or oxygen-containing polymer) and this char is foamed by gases released during decomposition of a nitrogen compound. The acid component is typically phosphoric acid or a suitable derivative such as ammonium polyphosphate. Typical carbonifics include pentaerythritol and other polyols. Common spumifics include urea, melamine, and dicyandiamide. Commercial intumescent systems containing the catalyst, carbonific, and spumific are available.

A coordinated sequence of chemical and physical reactions is necessary for a good intumescent coating to form. The timing of acid release, degradation of the carbonific and evolution of gas must be closely coupled. In addition, the viscosity of the mass while these processes occur must be such that the small bubbles produced result in a multicellular char that eventually gels and solidifies. Polyamides [5] and polyolefins, such as polypropylene (PP) [6], are some of the resins where additives promoting intumescence have been found to be effective flame retardants.

Other additives function as flame retardants in the condensed phase, not by forming an intumescent layer, but by depositing a surface coating which insulates the polymer from the heat source and retards the evolution of additional fuel. Some silicone flame retardants for polyolefins are thought to deposit silicon dioxide (sand) on the polymer surface [7]. Resorcinol diphenylphosphate (RDP) is an organophosphate which provides flame retardancy in the condensed phase by a unique mechanism. RDP apparently catalyzes the Fries rearrangement of several resins (PC, PC/ABS, PPO) to give phenolic-containing decomposition products. These products can undergo transesterification with RDP to form non-volatile, non-combustible, phosphorus species on the surface of the resin [8]. This "surface barrier" may inhibit the diffusion of combustible gases to the flame. Aromatic sulfonate salts are also thought to impart flame retardancy to PC by catalyzing the Fries rearrangement [9].

The largest volume flame retardant, alumina trihydrate (ATH), functions in the condensed phase, not as a char former or protective-layer former, but as a heat sink and a source of non-combustible gas (H_2O) for fuel dilution. ATH starts to decompose at 230°C and eventually loses 34.5% of its mass as water vapor. Magnesium hydroxide decomposes at higher temperature (340°C) with a 31% mass loss. ATH and magnesium hydroxide also decompose endothermically and remove heat from the condensed phase which decreases

rate of polymer decomposition. The enthalpy of decomposition for alumina trihydrate is 280 cal/mole while that for magnesium hydroxide is -328 cal/mole. Substantial quantities of these additives are needed to impart flame retardancy to a resin. A resin formulation containing 40 to 60% (by weight) ATH is typical.

Melamine and some melamine derivatives appear to provide flame retardancy through a number of different mechanisms [10]. Melamine sublimates rather than melts and can cool the heat sink) a polymer such as polyethylene (PE) when the plastic is subjected to heat. Melamine vapor, having a high nitrogen content, can act as an inert diluent in the flame. One in the flame, the melamine can dissociate, providing another heat sink. Melamine carbonate also functions as a heat sink and an inert gas source in polyamides, while melamine polyphosphate provides fire retardancy in an intumescent manner [11].

The styrenic polymers melt, drip, and depolymerize to form volatile monomers, dimers, and trimers when exposed to heat. Typically, these polymers require a flame retardant function in the gas phase rather than the condensed phase. A possible exception is polystyrene foam, where hexabromocyclododecane (HBCD) is a common flame retardant additive. HBCD is thought to promote a decrease in the polymer molecular weight and viscosity, resulting in the foam shrinking away from the combustion source [12].

Flame retardants operating in the gas phase interrupt the combustion chemistry of the fire. During combustion, polymer fragments interact with oxygen and other highly reactive species in a chain reaction to form oxygen radicals, hydroxyl radicals, and hydrogen radicals. Certain plastic additives, mainly those containing halogen or phosphorus, can chemically interact with these radicals to form less energetic species and, in effect, interrupt the chain propagation necessary for fire initiation or continuation.

Some important reactions in the combustion of hydrocarbons involve reactions 12.1, 12.2 and 12.3.



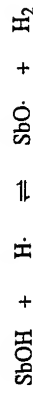
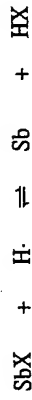
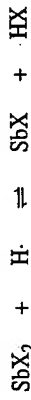
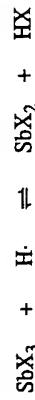
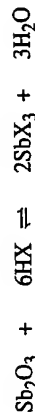
The hydrogen-oxygen reaction can be interrupted, the combustion of the fuel can be retarded [13]. Hydrogen halides are efficient flame quenchers and their effectiveness follows the order $HI > HBr > HCl > HF$ on a molar basis. The flame quenching effects are thought to be caused by inhibition of chain branching reactions 12.1 and 12.2 via the action of hydrogen halide to produce the less reactive halogen radical (reactions 12.4 and 12.5).



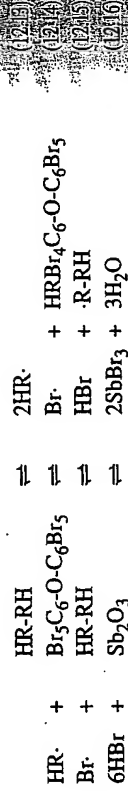
Many chlorinated and brominated flame retardants, especially aliphatic types, release HX on heating. However, in practice, it has been found that improved flame retardancy often

results from halogenated materials when metal oxides, such as antimony oxide, are added. In World War II, a combination of chlorinated paraffin, antimony oxide, and binders was used as a fire retardant and waterproof treatment for canvas. The use of organohalogen antimony oxide is a true case of synergism because antimony oxide by itself imparts minimal flame retardancy to most materials.

Many investigators agree that the formation of volatile antimony species (antimony trihalide, antimony oxyhalide) is responsible in great part for the synergistic effect of the action of halogen-antimony oxide has been explained on the basis of two separate flame inhibition effects [14]. The halogen compound decomposes on heating to form HX which reacts with antimony oxide to form volatile antimony halide. The antimony halide then interrupts the combustion process by removing hydrogen radicals in the flame by a multistep process. The antimony oxide-catalyzed recombination of hydrogen radicals prevents the second mode of inhibiting combustion.



Organohalogen compounds that do not generate HX upon heating rely on the polymer to initiate the reaction with antimony oxide. For example, high impact polystyrene (HIPS) formulated with decabromodiphenyloxide and antimony oxide can generate hydrocarbon radicals at high temperatures. The radical can react with the organohalogen to initiate formation of antimony tribromide, leading to combustion inhibition [15] (reactions 12.15 and 12.16).



Some phosphorus flame retardants can also be effective in the gas phase. Volatile molecules such as triphenylphosphate can fragment in the flame to give small, phosphorus-containing radicals that can combine with hydrogen radicals to help quench the flame.

Common Name (Trade Name)	Structure	Physical Properties	Typical Use
Dibromoterephthalglycol (DSB FR-522)		m.p. = 109–110 °C b.p. = 134 °C (1 mm)	PUR UPE
Ethylene-bis (5,6-dibromo- norbornane-2,3- dicarboximide) (Saytex® BN-451)		m.p. = 294 °C	PP
Ethylene-bis(tet- rabromophthal- imide) (Saytex® BT-93)		m.p. = 450 °C	HPS PBT PE, PP
Halogenated Polyetherpolyols (IXOL® B350)		mixture, liquid	PUR
Hexabromo- cyclododecane (Saytex® HP- 900; GLCC CD- 75P; DSB FR- 1206)		m.p. = 175–195 °C (mixture) Isomer 1, m.p. = 170–172 °C Isomer 2, m.p. = 170–172 °C Isomer 3, m.p. = 203–205 °C	PS Foam
Octabromo- diphenyloxide (DSB FR-1208; GLCC DE-79)		mixture, m.p. = 70–150 °C	ABS
Octabromotri- nethylphenylindane (DSB FR-1808)		m.p. = 230–250 °C	HPS ABS
Pentabromo- diphenyloxide (GLCC DE-71)		mixture, m.p. < 30 °C	PUR
Poly(dibromosty- rene) (GLCC PDBS-80)		m.p. = 210–230 °C	PBT PET PA
Poly(pentabromo benzylacrylate) (DSB FR-1025)		m.p. = 190–210 °C	PBT
Resorcinol Diphenylphos- phate (RDP)		mixture, liquid	PC/ ABS PPO/PS

Common Name (Trade Name)	Structure	Physical Properties	Typical Use
Tetrabromo- bisphenol-A (Saytex® CP-2000; GLCC BA-59; DSB FR-1524)		m.p. = 179–181 °C	Epoxy resins, ABS
Tetrabromo- bisphenol-A, propyl ether) (Saytex® HP-800; GLCC PE-68; DSB FR-3100)		m.p. = 90–100 °C	PP
Tetrabromo- bisphenol-A, carbonate oligo- mer) (GLCC BC-52; GLCC BC-58)		m.p. = 210–260 °C	PBT
Tetrabromo- phthalate Diols (Saytex® RB-79; GLCC PHT4- DIO)		mixture, liquid	PUR
Tetrabromo- phthalic anhydride (Saytex® RB-49; GLCC PHT4)		m.p. = 270–276 °C	UPE
Tetrabromo- phenoxylbenzene (Saytex® S-120)		m.p. > 350 °C (decomp)	PET, PA, PBT
Triphenyl- phosphate		m.p. = 50–52 °C; b.p. = 244 °C/ 10 mm	PC/ ABS, PPO, PS

ABS = acrylonitrile/butadiene/styrene

PS = expandable polystyrene

HPS = high impact polystyrene

PE = polyamide

PET = poly(ethylene)terephthalate

PBT = polycarbonate

PA = polyethylene

PHT = poly(ethylene)terephthalate

PP = polypropylene

PPO = polyphenylene oxide

PU = polyurethane

PC = polychloride

PB = unsaturated polyester

12.4 Typical Flame Retardant Formulations

The world of plastics can be separated into two general classes: thermoplastics and thermosets. The variety of flame retardants applicable to these two major groups is quite varied. Thermoplastics (ABS, PC/ABS, HPS, EPS, PP, PE, PA, PC, PBT) can usually be formulated with halogen-containing and non-halogen containing additives that increase the ignition resistance of the resin to high fire safety standards, such as 5VA or V-0 by the UL-94 test. The actual use of the additive depends on the fire rating desired and the composition and amount of other additives in the resin. Table 12.1 lists flame retardants typically used with specific thermoplastic resins.

Thermoset plastics (epoxy, unsaturated polyester, PUR) are commonly treated by adding flame retardants that chemically react with a resin precursor. Some non-reactive additive, however, are also used. Table 12.2 lists flame retardants typically used with thermoset resins.

Table 12.1 Commonly used flame retardants for specific plastics

Resin	Flame Retardant	FR Level (wt%)	Synergist (wt%)
ABS	Octabromodiphenyl oxide	18-22	4-8
	Tetrabromobisphenol-A	18-22	4-8
	bis(Tribromophenoxy)ethane	20-24	4-8
	Brominated Epoxy Oligomers	21	5-7
EPS	Hexabromocyclododecane	2-4	
HPS	Decabromodiphenyl oxide	12	4
	Decabromobiphenyl	12	4
	Decabromodiphenylethane	12	4
	Ethylene-bis-tetrabromophthalimide	12	4
	Octabromotrimethylphenylindane	15	4
Polyamides	Ammonium Polyphosphate	13	5
	Brominated Polystyrene	17	5
	Dechlorane Plus*	18	9
	Poly(dibromostyrene)	18-22	4-5
	Tetradeabromodiphenoxybenzene	14	5
	Red Phosphorus	7-8	5
	Magnesium Hydroxide	60	3
	Poly(pentabromobenzylacrylate)	13	
PBT	Tetradeabromodiphenoxybenzene	10	5
	Dechlorane Plus	16	5
	Decabromodiphenylethane	10	5
	Brominated Polystyrene	12	5
	Poly(dibromostyrene)	16-18	4-5
	Poly(pentabromobenzylacrylate)	11	5
	Tetrabromobisphenol-A, carbonate oligomers	17-19	4-5

Table 12.1 Continuation

Flame Retardant	FR Level (wt%)	Synergist (wt%)
Alkali metal organosulfonate	1	
Tetrabromobisphenol-A, carbonate oligomers	8-10	
Resorcinol Diphenyl Phosphate Triphenylphosphate	14 10	
Decabromodiphenyl oxide	21	7
Tetrabromobisphenol-A, bis(2,3-dibromopropyl ether)	6-15	3-5
Alumina trihydrate	60	

*Supplier List for tradename ownership

Table 12.2 Common flame retardants used with thermoset plastics

Flame Retardant	FR Level
Tetrabromobisphenol-A	18 wt% Br
Tetrabromophthalic Anhydride Chlorendic Acid/Anhydride	10-22 wt% Br 15-29 wt% Cl
Tetrabromophthalate Diols Pentabromodiphenyl oxide Dibromoneopentylglycol	15-28% 6-18% 5-15%

largest used with many halogenated flame retardants is antimony oxide. The use of antimony has been driven by its relatively low cost and its effectiveness in reducing the effect of halogen-containing material required to meet a particular standard. Other elements such as sodium antimonate, iron oxide, zinc borate, zinc phosphate, and zinc stannate have also been used in a variety of plastics. Small amounts of Teflon¹ are often incorporated into the formulation to retard dripping.

For thermoplastics containing non-reactive flame retardants, the components are mixed and the extrudates are pelletized and molded or blown into the desired shape. For thermosets, the mixing and heat treatment may be accomplished in a Brabender batch mixer. Specimens can be formed by compression molding, injection molding, or extrusion. For thermosets requiring a reactive flame retardant, small scale reactions are often carried out mechanically in suitable containers to generate test products.

¹Registered trademark of DuPont & Co., Inc.

12.5 Evaluation of Flame Retardants

The testing of formulations containing flame retardants can be done on a laboratory scale with a simple Bunsen burner or on a larger scale using an actual controlled fire, such as practiced at one of the fire testing institutes (Southwest Research Institute, Underwriters Laboratory, etc.). For rapid evaluation of flame retardant effectiveness, many researchers in the USA determine the UL-94 rating and the limiting oxygen index (LOI). In Europe, the German DIN 4102, the British BS 476 Part 7, and the French NF P 92-501 are used for building materials and to assign flammability ratings.

The "Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-Like Combustion of Plastics (Oxygen Index)", or LOI, has the advantage of providing numerical data regarding a formulation containing a flame retardant. The procedure involves burning a vertically supported test specimen in a mixture of oxygen and nitrogen that is flowing upwards through a transparent chimney. The test material is ignited at its upper end and the burning is observed in O_2/N_2 mixtures of varying composition. In general, the higher the oxygen concentration required for combustion, the more resistant the formulation is to ignition. For a resin such as HIPS, a formulation which gives a LOI of 28 or more can be considered to be effectively flame retarded. Unfortunately, no strong correlation has been observed between the LOI and the performance of the plastic in actual fires. The LOI method has been standardized by the American Society for Testing and Materials as ASTM D 2863 and by the International Organization for Standardization as ISO 4589-2. The LOI can be used to investigate the mechanism of flame retardancy by comparing results obtained from N_2/O_2 mixtures with those obtained from N_2/CO_2 mixtures. A flame retardant operating in the gas phase should have more of an effect on LOI than on LNOI because the different nature of the flame. A flame retardant operating in the condensed phase should show the same behavior in both systems. The comparative testing is a useful indicator, but it is not conclusive.

The preferred rapid test for flame retardancy effectiveness for many additives is the Underwriters Laboratory UL-94. This test assigns a V-0, V-1, or V-2 rating to a plastic. The V-0 classification is typically mandated for those applications where the flame retardant requirement is most severe. In the UL-94 test, a sample of specified dimensions is suspended vertically over a piece of surgical cotton. The sample is heated with a Bunsen burner for 10 seconds followed by a second 10 second application after the first test sample flame extinguishes. Five identical samples are evaluated in each UL-94 test. The samples are classified V-0, V-1, or V-2 based on the following criteria:

- V-0
 - afterflame time < 10 sec
 - sum of afterflame times (10 flame applications) ≤ 50 sec
 - no burning drips igniting the cotton
 - samples do not burn completely to the clamp
 - afterglow after removal of ignition ≤ 30 sec

– afterflame time < 30 sec
 – sum of after flame times (10 flame applications) ≤ 250 sec
 – no burning drips igniting the cotton
 – samples do not burn completely to the clamp
 – afterglow after removal of ignition source ≤ 60 sec

– afterflame time < 30 sec
 – sum of afterflame times (10 flame applications) ≤ 250 sec
 – ignition of cotton by burning drips
 – samples do not burn completely to the clamp
 – afterglow after removal of ignition source ≤ 60 sec

– the sample thickness (3.2mm, 1.6mm) is specified as part of the rating.

A rigorous test in the UL-94 series is the 94-HB. The sample scribed with marks 50 mm and 102 mm from one end is mounted horizontally, and the Bunsen flame is applied for 30 seconds. The extent of the burning is measured and ratings are assigned on the basis of the mean values from three determinations:

- burning rate between marks ≤ 38 mm/min
- burning rate between marks ≤ 76 mm/min
- extinguishment occurs before the 102mm mark.

The variation of the UL-94 test is the UL-94 5V. This test gives comparative burning characteristics of different samples, but the main emphasis is whether burn-through occurs. The procedure involves applying a 125 mm flame to the corner of a test specimen five times for five second intervals, recording the afterflame and afterglow times, and observing whether the flame burned through the sample. Material classified as 5VA has a combined afterflame and afterglow time of less than 60 seconds with no burn-through of the test sample. A 5VB classification indicates that the sample has a combined afterflame and afterglow time of less than 60 seconds but exhibits burn-through.

Real methods have been published in an attempt to standardize the UL-series of tests. ASTM D 635 describes UL-94HB; ASTM D 3801 describes UL-94 V-0; ASTM D 4804 describes UL-94 V-0 for flexible plastics; and ASTM D 5048 describes UL-94 5V. ISO 9773 combines the UL-94 HB and V-0 tests; ISO 9773 equates to ASTM D4804; and ISO 9773 is equivalent to ASTM D5048.

A cone calorimeter is more frequently used to evaluate flame retardant formulations. In a small scale test, a sample (typically 102 mm x 102 mm x 12.7 mm) is subjected to thermal radiation (heat flux) from a cone-shaped heater under a high flow of air. The gases created by heating the sample are ignited with a spark and the mass rate loss of the sample is obtained by monitoring the weight change with time. Exit gases such as CO , CO_2 , and H_2O are measured using gas analyzers. The rate of heat release is calculated on the basis of oxygen consumption.

Different formulations can be conveniently compared in a short time using the cone calorimeter. The principal advantage of this equipment is that much of the data gathered from cone measurements correlates with actual fires. For example, heat flux and heat release rate data are known for wire and cable and wall coverings. The significant disadvantage of the cone is the initial expense of the equipment or the inconvenience of contracting a laboratory to perform the testing. The measurement of heat release with the cone calorimeter has been standardized as ASTM E 1354 and ISO 5660-1. These two tests differ slightly in that ASTM E 1354 determines smoke obscuration as well as heat release and ignitability.

Full scale tests normally involve the finished article. Some common procedures are the Steiner Tunnel Test (ASTM E 84), room corner tests, and the CAL 133 Test. The Steiner Tunnel Test evaluates the flame spread potential of such products as electrical cable wall coverings, and insulation foam. The test specimen is attached to the ceiling of the tunnel and then exposed to flames from a gas burner for 10 minutes. The maximum flame spread, temperature, and smoke are measured. The flame spread index, which is a function of the flame spread versus time, is compared to the corresponding data generated from real life flooring and non-asbestos mineral fiber.

ISO 9705 contains a variety of procedures for carrying out room corner tests. With this method, three walls of a small room are lined with test material and irradiated with a gas burner of specific power from a specific location. The principal measurement is oxygen consumption. The actual evaluation of the effectiveness of the flame retardancy is whether flames can reach the outer extremities of the test material and whether flashback of the room occurs. ISO 9705 is being used to identify the limits for the seven classes (EUROCLASSES: A1, A2, B, C, D, E, F) of European wall and ceiling linings used in building products. The products will be marked to indicate whether the flame retardancy meets the highest standard (A1) or the lowest (F).

A new test procedure, the Single Burning Item (SBI), is also being developed for classifying building products in a harmonized European system. With the SBI, two test samples (500 mm x 1500 mm and 1000 mm x 1500 mm) are mounted in a corner configuration where they are subjected to a gas flame ignition source. The heat release rate and the smoke production rate from the fire are measured. Properties such as the occurrence of burning droplets/particles and flame spread are visually observed [16].

The CAL 133 Test is used in the USA almost exclusively with upholstered furniture. A fire source is directly applied to the article. Visual examination and measurements of such parameters as smoke, heat, and gas release can be used to evaluate the effectiveness of the component parts of the furniture in resisting fire.

12.6 Technological Trends

Future developments in flame retardants may well be driven by the search for products that meet the classic definition of a preferred flame retardant (inexpensive, easy to use, minimal effect on the physical properties of the resin, etc.), and are more "environmentally friendly" (recyclable, no potential to produce corrosive or toxic materials, etc.). Organohalogen and

inorganic compounds are now the world's dominant flame retardants in terms of sales and total volume. Many of the inorganic flame retardants, although seemingly "environmentally friendly", dramatically affect the physical properties of the plastic. The organohalogen compounds have shown consistent growth over the past 20 years, especially with exponential increases in the sales of computers and other electronic equipment. However, the potential for the generation of corrosive gases during combustion and concerns in Europe about exposure to ultratrace halogen-containing contaminants have led to considerable interest in alternative methods of flame retardancy.

Among the organobromine flame retardants, the brominated diphenyloxides (Pentabromodiphenyl oxide, Octabromodiphenyl oxide, Decabromodiphenyl oxide) have been the focus of numerous industry, governmental, and academic investigations. Brenner found that this class of polybrominated dibenzodioxins (PBDDs) and polybrominated dibenzofurans (PBDf) were emitted during the processing of PBT resin with decabromodiphenyl oxide and antimony oxide [17]. The brominated dibenzodioxins and brominated dibenzofurans are thought to have toxicity similar to their chlorinated analogs. Laboratory experiments by Jumper [18] and Lahaniatis [19] indicated that burning formulations containing brominated diphenylethers could produce measurable quantities of PBDD/PBDFs. This suggested that a halogenated electronic fire might be a potential source of dioxins. Other halogenated flame retardants such as hexabromocyclododecane, ethylene-bis-tetrabromophthalimide, and brominated polystyrene do not appear to generate these contaminants upon heating [20], but laboratory studies with the brominated diphenylethers have led to questions about all organohalogen flame retardants.

Through analysis of decabromodiphenyl oxide has shown that it contains none of the toxic 2,3,7,8-substituted PBDD/PBDFs at concentration levels required by the US Environmental Protection Agency (EPA) D/F Test Rule [21]. Nonetheless, the German chemical industry has adopted a voluntary ban on brominated diphenylethers. All of the halogenated flame retardants sold in Germany must meet stringent requirements on PHDD/PHDFs concentrations. For the organobromine compounds, German legislation (Chemicals Banning Ordinance) prohibits marketing goods which contain more than 1 µg/kg of the sum of

2,3,7,8-tetrabromodibenzodioxin
2,3,7,8-tetrabromodibenzofuran
2,3,7,8-pentabromodibenzodioxin
2,3,7,8-pentabromodibenzofuran
2,3,4,7,8-hexabromodibenzodioxin
2,3,6,7,8-hexabromodibenzodioxin
2,3,7,8,9-hexabromodibenzodioxin
2,3,7,8-pentabromodibenzofuran.

The German Chemicals Banning Ordinance has no provisions addressing the production of halogenated dibenzodioxins or polyhalogenated dibenzofurans from the burning of formulations containing halogenated flame retardants. Other regulations govern incinerator emissions. Interestingly, studies have shown that the combustion of municipal waste

containing added halogenated material does not increase difficulty in meeting regulatory standards.

Brominated diphenylethers, and by implication, halogenated flame retardants, have also undergone additional scrutiny by Scandinavian countries, especially Sweden. Partially brominated diphenylethers, particularly terabromo- and pentabromo-substituted, have been detected in breast milk [22a], bird's eggs [22b], and marine life [22c]. Levels are considerably below those of DDT and PCBs, but the presence of the contaminants has raised questions about their origins. Whether they arise from organisms which produce organohalogens or from anthropogenic sources remains to be determined. Emissions of partially brominated diphenylethers from electronic enclosures, such as televisions and computers, is unlikely because the commonly identified contaminants, 2,2',4,4'-tetrabromodiphenylether and 2,2',4,4',5-pentabromodiphenylether, are not the major components of the flame retardants used for these products. A more probable source is point source emissions from manufacturers and users.

No national or international regulations prohibit or regulate the use of brominated flame retardants. Risk assessments have concluded that the benefits of fire protection are significant and that the possible detrimental effects to humans are minimal. Various nations, however, have adopted voluntary "eco-labels" which certify that certain ingredients unacceptable to the issuing organization are absent from the product. Labels such as the "Blue Angel" and the "White Swan" are generally not granted to products containing organohalogens, other than organofluorine compounds (e.g. Teflon).

The perceived concerns about halogenated flame retardants, and halogen-containing compounds in general, have stimulated the search for non-halogenated flame retardants, particularly in areas related to electronic enclosures. Some success has been achieved. Halogen-free FR-grades of PC/ABS, polyamide, and PC, mainly based upon phosphorus additives, are offered by several suppliers. The premium cost and the deficiencies in physical properties of these resins, however, has stimulated further research. Recently promising new PC resin containing a silicone-based flame retardant has been introduced [23]. The flame retardant is very effective in retarding the combustion of the PC and the physical properties of the FR resin are very close to the PC resin itself.

Besides the additive approach, researchers have been designing plastics that are inherently ignition resistant. A polyphenylene oxide (PPO)/polystyrene blend can be used to improve flame retardancy of pure polystyrene without the use of additional additives [24]. A new self-extinguishing epoxy resin that contains no added flame retardant has also been reported [23]. A polycarbonate-siloxane copolymer has been introduced that has excellent flame retardancy properties and almost the same physical properties as a typical polycarbonate resin [25].

However, a halogen-free, cost and performance effective flame retardant for one of the most widely used resins, HIPS, still eludes researchers. Further research with organophosphinates, which appear to have promise as flame retardant additives for ABS [26], to identify some candidate molecules for this market.

Research in the area of nanocomposites may yield a generation of flame retardant additives which are effective and environmentally friendly. Already, workers at Cornell University and National Institute of Standards and Technology (NIST) have demonstrated that intercalated polymer-clay nanocomposites prepared from polystyrene, nylon-6, and polyethylene-graft-maleic anhydride have substantially lower peak heat release rates (HRR) than the pure polymers [27]. The HRR reduction for polystyrene was comparable to that achieved with a very high loading of decabromodiphenyl ether/antimony oxide, a common flame retardant for polystyrene. The advantages of nanocomposites are the fact that small (30-60%) loadings are used to impart flame retardancy and the physical properties of the resin are not adversely impacted. In the case of nylon-6, the properties actually seemed to be improved.

For polymer-clay nanocomposites can be prepared by combining the appropriately modified clay and polymer. For example, melt blending polystyrene with bis(dimethyl)-[octadecyl]ammonium-exchanged montmorillonite, yields a nanocomposite with an unrelated structure. The treatment of the clay with an alkylammonium salt removes the ammonium and results in an organophilic instead of a hydrophilic clay. Cone calorimeter measurements suggest that the flame retardancy of these resin-clay nanocomposites is improved by thermal decomposition to form a char layer that acts as an insulator and slows escape of potential fuel. One objective that still remains to be met with the nanocomposites, however, is the achievement of a V-0 rating in the common UL-94 test.

Another area of interest are additives that promote cross-linking in plastics when they are exposed to conditions normally resulting in thermal decomposition [28]. The cross-linking will decrease the fuel volatility and possibly provide a char layer as a protective barrier.

127 List of Trade Names, Manufacturers/Suppliers

Following is a list of manufacturers and suppliers of flame retardants and the trade names for their products. No claim is made that this list is complete.

Manufacturer/Supplier	Trade Name/Chemical Name
ICI Nobel Chemicals bv ICI Polymer Chemicals Stationsplein 1118 AF Amersfoort The Netherlands	Fyrol; Fyrolflex; Phosflex/ Organophosphates
Vencor Corporation 85 Florida Boulevard Palm Breeze, LA 70650 USA	Saytex; NcenX/Organobromides; Organophosphates

Manufacturer/Supplier	Trade Name/Chemical Name
Alcoa 201 Isabella Street at the 7th Street Bridge Pittsburgh PA 15212-5858 USA	Alumina Trihydrate
Chemische Fabrik Budenheim Rheinstraße 27 55257 Budenheim Germany	Budii/Ammonium Polyphosphate, Melamin Derivatives
Clariant GmbH Industriepark Höchst; Geb. C660 D 65926 Frankfurt am Main Germany	Exolit/Phosphorus Compounds
Cytec Industries Inc. Five Garret Mountain Plaza West Paterson, New Jersey 07424 USA	Cyagard; Aerogard/ Organophosphates/ Derivatives
Dainippon Ink & Chemicals Inc. 3-7-20; Nihonbashi Chuo-ku Tokyo 103; Japan;	Prathem/ Brominated Epoxy Oligomers
Dead Sea Bromine Group Makleff House 12 Kroizer St. P.O. Box 180 Beer Sheva 84101 Israel	Organobromides, Magnesium Hydroxide
DSM PO Box 6500 6401 JH Heerlen The Netherlands	Melapur/Melamine/Derivatives
DuPont Dow Elastomers L. L. C 300 Bellevue Parkway Suite 300 Wilmington Delaware 19809 USA	Tyrit/Chlorinated Polyethylene
Great Lakes Chemical Corporation One Great Lakes Blvd. West Lafayette Indiana 47996 USA	Firemaster; Bloomguard; Reofos; Kronite; Reomol; Timonox/Organobromides; Organophosphates; Antimony Oxide
Huber Engineered Minerals Northside Parkway Atlanta Georgia 30327 USA	Alumina Trihydrate

Manufacturer/Supplier	Trade Name/Chemical Name
Mano Marietta Magnesia Specialties 710 Wycliff Road Greenville North Carolina 27607 USA	Magnesium Hydroxide
Oxidental Petroleum Corporation 189 Wilshire Boulevard Los Angeles California 90077-4201 USA	Dechlorane Plus/Organochlorides Antimony Oxide
Phos-Chem, Inc. Phosphorus & Performance Derivatives CN 500 Canbury, NJ 08812-7500 USA	Angard; Antiblaze/Organophosphates
Solway S. A. Rue du Prince Albert; 44 1050 Bruxelles Belgium	IXOL/Organohalides
Phos-Chem 100 Olive Boulevard P.O. Box 66760 St. Louis Missouri 63166-6760 USA	Phos-Chek/Ammonium Polyphosphate
Phos-Chem Corporation 17 Alaska I-chome Hawato-ku Hawaii 96710-107-8451;	Organobromides, Magnesium Hydroxide
Phos-Chemical Corporation P.O. Box 16344 20 Broome Road Greensboro North Carolina 27406 USA	FRP/Organobromides
Phos-Chem Inc. 2877 Tournay Road Hawato-ku California 94555 USA	Firebrake/Boron Compounds

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3 Chemical Blowing Agents

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11 Introduction

Chemical blowing agents are additives used in the manufacturing of foamed plastics. Most blowing agents are organic chemicals, although some inorganic compounds are in use, also. These additives act by causing blowing gas to evolve by thermal decomposition, which then forms the foamed structure in the polymer matrix.

The main reason for manufacturing foamed plastics is their greatly reduced density, which reduces weight of the finished material and decreases costs. Additional or improved properties are another benefit, including improved heat and sound insulation, improved mechanical properties, higher shock absorption, higher rigidity of integral materials, reduction of sink spots in heavy-section injection molded parts, and decorative effects.

12 Basic Principles and Function of Blowing Agents

Various blowing agents used to foam polymers can be classified according to their method of liberating the blowing gas, i.e., they can be divided into chemical blowing agents (pure chemical blowing agents). Chemical blowing agents may be chemical individuals (pure monomers), blends, or preparations diluted with functional additives. During the foaming process at elevated temperatures, chemical blowing agents undergo chemical reactions (usually decomposition) that liberate the blowing gas. Most chemical blowing agents are

solid blowing agents do not undergo chemical transformation. The blowing gas is liberated by physical processes, typically by vaporization of a low-boiling liquid or by release of pressure in a compressed gas. Usually, physical blowing agents are liquids.

Chemical blowing agents deal exclusively with chemical blowing agents. Chemical blowing agents are divided into three groups, according to their mode of action:

Compounds that split off the gaseous products as the result of an irreversible thermal decomposition. The well known organic chemical blowing agents belong to this group. This chapter describes ADC, TSH, OBSH, TSSC, 5-PT, DNPT (for full names and formulae see Section 13.3). Their mode of decomposition at elevated temperatures may be summarized as follows:



These reactions are typically first order and the liberated gaseous fragments are N_2 , CO , and NH_3 .